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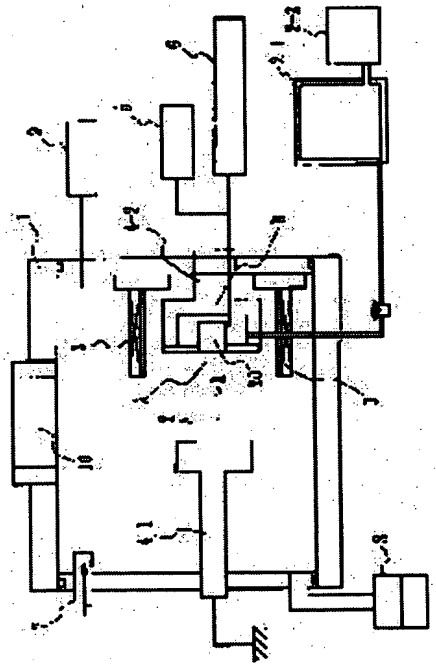
## (54) THIN FILM DEPOSITION METHOD AND THIN FILM DEPOSITION APPARATUS

(57)Abstract:

PROBLEM TO BE SOLVED: To provide an apparatus for depositing a thin film on an inner wall of tubular members in an easy manner without depending on the inside diameter and the number of the tubular members.

SOLUTION: A rear part in the longitudinal direction X of the tubular member 20 is evacuated by a pressure difference generating means 2 comprising a pressure adjustment tank 2-1 and a pump 2-2. The pressure is set to ≤1/10 of the pressure in a forward part in the longitudinal direction X of the tubular member 20. Plasma reaction gas generated by applying the predetermined voltage from a DC power source 5 and a high-voltage pulse power source 6 to raw gas introduced in a film deposition chamber 1 from a gas introduction hole 7 is efficiently introduced into the tubular member 20 by utilizing the pressure difference in the forward part and the rear part in the longitudinal direction X of the tubular member 20. The plasma reaction gas is chemically synthesized on the inner wall of the tubular member 20 to manufacture a thin film.



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## CLAIMS

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[Claim(s)]
[Claim 1] While being the method of producing a thin film by plasma CVD on an internal surface of a tubular member and arranging said tubular member in predetermined plasma-CVD equipment Produce differential pressure before and after a longitudinal direction of said tubular member, and plasma reactant gas is made to flow in said tubular member according to said differential pressure. A thin film production method characterized by making said plasma reactant gas compound chemically, and producing said thin film on said internal surface of said tubular member.
[Claim 2] Differential pressure before and behind said longitudinal direction of said tubular member is the thin film production method according to claim 1 characterized by making it generated by setting a pressure of said longitudinal direction back section or less to 1/10 to a pressure of said longitudinal direction front section.
[Claim 3] A thin film production method according to claim 1 or 2 characterized by making it make it flow in said tubular member, having produced a predetermined magnetic field in said longitudinal direction of said tubular member, and catching said plasma reactant gas by said predetermined magnetic field.
[Claim 4] Said predetermined magnetic field is the thin film production method according to claim 3 characterized by making it converge in a direction perpendicular to said longitudinal direction of said tubular member so that it may become smaller than a bore of said tubular member.
[Claim 5] A thin film production method according to claim 3 or 4 that magnitude of said predetermined magnetic field is characterized by being more than 2.0x10-7/rT to a bore r of said tubular member.
[Claim 6] A thin film production method according to claim 1 to 5 which is made to produce predetermined electric field in said longitudinal direction of said tubular member, and is characterized by making it make said plasma reactant gas flow in said tubular member according to said predetermined electric field.
[Claim 7] A thin film production method according to claim 6 that magnitude of said predetermined electric field is characterized by being 20 - 200 kV/m.
[Claim 8] Said bore of said tubular member is the thin film production method according to claim 1 to 7 characterized by being 0.001-1mm.
[Claim 9] Said thin film is the thin film production method according to claim 1 to 8 characterized by consisting of diamond or diamond-like carbon.
[Claim 10] Thin film production equipment which is equipment which produces a thin film by plasma CVD on an internal surface of a tubular member, is made to produce differential pressure before and after a longitudinal direction of said tubular member to predetermined plasma-CVD equipment, and is characterized by establishing a differential pressure generation means by which plasma reactant gas was made to flow in said tubular member according to said differential pressure.
[Claim 11] Said differential pressure generation means is thin film production equipment according to claim 10 characterized by setting a pressure of said longitudinal direction back section of said tubular member or less to 1/10 to a pressure of said longitudinal direction front section.

[Claim 12] Thin film production equipment according to claim 10 or 11 characterized by establishing a magnetic field generation means it was made to make flow in said tubular member, having produced a predetermined magnetic field in said longitudinal direction of said tubular member, and catching said plasma reactant gas by said predetermined magnetic field to said predetermined plasma-CVD equipment.

[Claim 13] Said magnetic field generation means is thin film production equipment according to claim 12 characterized by completing said predetermined magnetic field in a direction perpendicular to said longitudinal direction of said tubular member so that it may become smaller than a bore of said tubular member.

[Claim 14] Thin film production equipment according to claim 10 to 13 which is made to produce predetermined electric field in said longitudinal direction of said tubular member, and is characterized by establishing an electric-field generation means by which it was made to make said plasma reactant gas flow in said tubular member according to said predetermined electric field to said predetermined plasma-CVD equipment.

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## DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[The technical field to which invention belongs] This invention relates to the thin film production method and thin film production equipment to the internal surface of a tubular member which can be suitably used as a wear-resistant thin-layer-coating means in detail about the thin film production method and thin film production equipment.
[0002]
[Description of the Prior Art] A hard film, for example, a diamond film, and a diamond-like carbon film are formed on a predetermined base material, and things are performed for giving abrasion resistance to said predetermined base material. And in recent years, the attempt which forms said hard film to the internal surface of the tubular member which can consider the application to many products is made.
[0003] Formation of a hard film introduces material gas, such as methane, in a plasma fission reactor with carrier gas, such as hydrogen gas, etc., by microwave, a RF, etc., it excites said material gas, generates plasma reactant gas, and is carried out using the so-called plasma-CVD method make a chemical reaction perform on said predetermined base material. However, although a plasma-CVD method can form a predetermined hard film in homogeneity to the member of plate-like part material or a configuration simple in addition to this, since said plasma reactant gas to each component surroundings being crowded of a method became inadequate to the member of complicated configurations, such as an internal surface of a tubular member, it was not able to form a uniform hard film.
[0004] In view of this point, the electrode which becomes the interior of a tubular member from graphite material is arranged in JP,62-136569,A, and to form plasma reactant gas directly from material gas inside said tubular member is tried. According to this method, since said a lot of plasma reactant gas can be supplied on the internal surface of said tubular member, a comparatively thick hard film can be formed on said internal surface at simple and homogeneity.
[0005]
[Problem(s) to be Solved by the Invention] However, it is necessary to prepare a graphite electrode smaller than the bore of a tubular member, and in the above-mentioned method, if the bore of said tubular member becomes very small, the production will become very difficult. Moreover, if two or more tubular members tend to be prepared and it is going to form a hard film in coincidence to these internal-surfaces top, it will be necessary to prepare the graphite electrode according to the number of said tubular members. Consequently, while the configuration of the whole plasma-CVD equipment became complicated, there was a problem that the production production process of a hard film became very complicated.
[0006] This invention aims at offering a means to produce a thin film on the internal surface of said tubular member very simply, without being dependent on the magnitude of the bore of a tubular member, or its number.
[0007]

[Means for Solving the Problem] While this invention is the method of producing a thin film by plasma CVD and arranges said tubular member in predetermined plasma-CVD equipment on an internal surface of a tubular member which has a base in which opening was formed that the above-mentioned purpose should be attained Produce differential pressure before and after a longitudinal direction of said tubular member, and plasma reactant gas is made to flow in said tubular member according to said differential pressure. It is related with a thin film production method characterized by making said plasma reactant gas compound chemically, and producing said thin film on said internal surface of said tubular member.
[0008] Moreover, this invention relates to thin film production equipment which is equipment which produces a thin film by plasma CVD on an internal surface of a tubular member which has a base in which opening was formed, is made to produce differential pressure before and after a longitudinal direction of said tubular member to predetermined plasma-CVD equipment, and is characterized by to establish a differential pressure generation means to by_which plasma reactant gas was made flow in said tubular member according to said differential pressure.
[0009] this invention persons inquired wholeheartedly that the above-mentioned purpose should be attained. Consequently, it found out that the above-mentioned purpose could be attained by forming differential pressure before and after a longitudinal direction of a tubular member which should form a predetermined thin film, and making plasma reactant gas which excited and obtained predetermined material gas in said tubular member using this differential pressure flow.
[0010] That is, in the conventional plasma-CVD method, after having introduced said predetermined material gas in equipment, exciting it and making plasma reactant gas generate, said plasma reactant gas was supplied on a predetermined part, for example, an internal surface of a tubular member, by the convection current of said material gas. On the other hand, he is trying according to a thin film production method and thin film production equipment of this invention, to prepare differential pressure before and after a longitudinal direction of said tubular member with a differential pressure generation means, as mentioned above.
[0011] Therefore, compared with a plasma-CVD method using the conventional convection current, a lot of plasma reactant gas can be supplied on an internal surface of said tubular member. Consequently, on an internal surface of said tubular member, said plasma reactant gas can be made to be able to react chemically enough, and the target thin film can be formed simply.
[0012] Thus, according to a thin film production method and thin film production equipment of this invention, since plasma reactant gas is introduced in a tubular member using differential pressure, when a bore of said tubular member is small enough, said plasma reactant gas can be introduced efficient, and thin film formation can be simply performed to an internal-surface top.
[0013] Moreover, since it is not necessary to prepare an electrode etc. for every tubular member, the target thin film can be formed on an internal surface of two or more tubular members at coincidence, and thin film production effectiveness can be raised greatly.
[0014] In a desirable mode of this invention, it is desirable to make it flow in said tubular member, establishing a magnetic field generation means, producing a predetermined magnetic field in a longitudinal direction of said tubular member, and catching said plasma reactant gas by said predetermined magnetic field. By this, since an inflow rate into a tubular member of plasma reactant gas increases, said plasma reactant gas can be more efficiently introduced in said tubular member.
[0015] Furthermore, it is desirable to form an electric-field generation means in this invention in other desirable modes, to produce predetermined electric field in a longitudinal direction of said tubular member, and to introduce said plasma reactant gas in said tubular member according to said predetermined electric field. Also in this case, since an inflow rate into said tubular member of said plasma reactant gas increases, said plasma reactant gas can be more efficiently introduced in said tubular member.
[0016] In addition, with the above-mentioned electric-field generation means, said material gas can be excited and plasma reactant gas can also be generated. In this case, since it is not necessary to establish an additional excitation means in order to generate plasma reactant gas, while a configuration of the whole equipment is simplified, a thin film production production process can be simplified.

[0017]
[Embodiment of the Invention] Hereafter, this invention is explained to details based on the gestalt of implementation of invention, making it connected with a drawing.
[0018] Drawing 1 is drawing showing an example of the thin film production equipment of this invention. The thin film production equipment shown in drawing 1 is equipped with the header tank 2-1 as a differential pressure generation means connected and formed in the membrane formation room 1 and this membrane formation room 1 and a pump 2-2, the coil 3 as a magnetic field generation means, and the anode plate 4-1 and cathode 4-2 as an electric-field generation means. An anode plate 4-1 is grounded and DC power supply 5 and the high-pressure pulse power supply 6 are connected to cathode 4-2.
[0019] Moreover, the pump 8 as an exhaust air means is formed in order to hold the inside of the gas installation hole 7 for introducing predetermined material gas into the membrane formation room 1, and the membrane formation room 1 to a predetermined degree of vacuum. Furthermore, a pressure gage 9 and an aperture 10 are formed, and it is constituted so that the monitor of the degree of vacuum in the membrane formation room 1 and the condition of plasma reactant gas can always be carried out. The tubular member 20 is fixed and installed [ above cathode 4-2 ].
[0020] Thin film production of a up to [ the internal surface of the tubular member 20 ] is the following, and is made and carried out.
[0021] More nearly first than the gas installation hole 7, after exhausting the inside of the membrane formation room 1 to a predetermined degree of vacuum with a pump 8, predetermined material gas is supplied in the membrane formation room 1. And it accompanies with exhaust air with a pump 8, and the inside of the membrane formation room 1 is held to a predetermined degree of vacuum. In addition, it acts as the monitor of the degree of vacuum with the pressure gage 9 formed in the membrane formation room 1.
[0022] Subsequently, impressing a predetermined DC bias by DC power supply 5, by impressing a predetermined pulse voltage from the high-pressure pulse power supply 6, said material gas is excited and plasma reactant gas is generated.
[0023] Subsequently, the four to cathode 2 perimeter in which the tubular member 20 was installed through the pressure regulation layer 2-1 from the pump 2-2 is exhausted, and differential pressure is produced before and after the longitudinal direction X of the tubular member 20. As for the differential pressure before and behind the longitudinal direction X of the tubular member 20, it is desirable to set up so that the pressure in the back section of the longitudinal direction X of the tubular member 20 may become 1/10 or less [ of the pressure in the front section of a longitudinal direction X ] and 1/100 more or less. By this, said plasma reactant gas can be more efficiently introduced in the tubular member 20.
[0024] The pressure in the membrane formation room 1 is before and after about ten to 2 Torr, and since the pressure of the front section A of the longitudinal direction X of the tubular member 20 also becomes about ten to 2 Torr order, specifically, the pressure of the back section B of the longitudinal direction X of a tubular member is controlled by the header tank 2-1 and the pump 2-2 to be set to about 10-3 - 10-4Torr.
[0025] Subsequently, a predetermined magnetic field is made to generate in the longitudinal direction X of the tubular member 20 by passing current to a coil 3. And as for this magnetic field, in the direction perpendicular to the longitudinal direction X of the tubular member 20 of Y, it is desirable to make it converge so that it may become smaller than the bore of the tubular member 20. By this, the inflow rate into the tubular member 20 of said plasma reactant gas can be increased more, and thin film formation of a up to [ the internal surface of the tubular member 20 ] can be carried out more simply and efficiently.
[0026] Moreover, when the bore of the tubular member 20 is set to r, as for the magnitude of said predetermined magnetic field, it is desirable that it is 2.0x10-7/rT. When the bore r of the tubular member 20 is 1.0mm, it is desirable that it is 1.0x10-4-3.0x10-4T, and, specifically, it is desirable to a pan that it is 2.0x10-4-3.0x10-4T. Since said plasma reactant gas can be caught more effectively and the inflow rate of said plasma reactant gas into the tubular member 20 increases by this, as mentioned

above, thin film formation of a up to [ the internal surface of the tubular member 20 ] can be carried out more simply and efficiently.
[0027] Furthermore, if it goes to an anode plate 4-1 from cathode 4-2, it originates in the DC bias and pulse voltage for exciting said material gas and generating plasma reactant gas, and predetermined electric field are generated. Therefore, said plasma reactant gas comes to flow in the tubular member 20 according to said predetermined electric field. Consequently, the inflow rate into the tubular member 20 of said plasma reactant gas increases, and thin film formation of a up to [ the internal surface of the tubular member 20 ] can be performed more efficiently.
[0028] As for the magnitude of said predetermined electric field, it is desirable that it is 20 - 200 kV/m, and it is desirable that they are further 20 - 100 kV/m. In the thin film production equipment shown in drawing 1 , although the voltage value impressed to cathode 4-2 from DC power supply 5 and the high-pressure pulse power supply 6 is mostly set to a certain within the limits that plasma reactant gas should be generated from material gas, said voltage value is suitably adjusted within the limits of this, and it sets up so that the magnitude of electric field may serve as a value of above-mentioned within the limits predetermined [ said ].
[0029] Since he is trying it not only to prepare differential pressure, but to generate said predetermined magnetic field and said predetermined electric field along with a longitudinal direction X before and after the longitudinal direction X of the tubular member 20 according to the thin film production equipment shown in drawing 1 as explained above, said plasma reactant gas can be made to flow in the tubular member 20 very efficiently. Therefore, a very efficient predetermined thin film can be formed on the internal surface of the tubular member 20.
[0030] The thin film production method and thin film production equipment of this invention are not limited about the configuration and size of the tubular member 20, but can be applied to the tubular member of all configurations and magnitude. Moreover, the tubular member 20 can also have the base in which opening was formed so that the inflow of the internal plasma reactant gas according to differential pressure may not be prevented. Since the amount of supply of the plasma reactant gas to the internal surface of said base increases when this base is prepared to the back section of the longitudinal direction X of the tubular member 20, it is comparatively thick and the thin film made into the purpose in said internal surface of said base can be formed efficiently.
[0031] However, by performing suitably control of differential pressure, and control of a magnetic field according to the magnitude of a tubular member in such a case, the thin film of sufficient thickness can be efficiently formed on the inside wall surface of the tubular member 20, and homogeneity and the target thin film can be efficiently formed on an inside wall surface and an inside bottom wall side by this.
[0032] According to the thin film production method and thin film production equipment of this invention, the target thin film can be efficiently formed even on the bore of 10mm or less, and the internal surface of a tubular member 1 moremm or less. Moreover, especially in the present condition, the target thin film can be efficiently formed on the internal surface of a tubular member 0.1mm or more the bore of 0.01mm or more.
[0033] Moreover, in the thin film production method and thin film production equipment of this invention, since the thin film is formed using differential pressure as mentioned above, and it is not necessary to prepare an electrode etc. for every tubular member, when two or more tubular members 20 have been arranged, in drawing 1 , the target thin film can be formed on the internal surface of the tubular member of these plurality at coincidence. Therefore, production effectiveness of a thin film can be made very high.
[0034] Moreover, it is not especially limited about the class of thin film formed on the internal surface of the tubular member 20. However, high abrasiveness can be given to the internal surface of the tubular member 20 by constituting said thin film from diamond or diamond-like carbon. Therefore, the tubular member 20 can be used as a predetermined slide member.
[0035]
[Example] Hereafter, an example explains this invention concretely.

(Example) In this example, it tried to form a diamond-like carbon film using production equipment as shown in drawing 1 on the internal surface of the tubular member by which the slit die opening regio oralis with a height [ of 0.1mm ] and a width of face of 40mm was formed in the base side and which is the bore of 1mm.
[0036] First, after fixing above the cathode 4-2 and installing said tubular member, the inside of the membrane formation room 1 was exhausted to the degree of vacuum of 10-5Torr with the pump 8. And the pressure in the membrane formation room 1 was set as 3.75x10-2Torr, having introduced CH4 gas by the flow rate of 20cm3/min, and exhausting with a pump 8 from the gas installation hole 7. Subsequently, the voltage of 1.5kV was impressed between an anode plate 4-1 and cathode 4-2, and CH4 gas plasma was made to generate from DC power supply 5 and the high-pressure pulse power supply 6. In addition, between an anode plate 4-1 and cathode 4-2, the electric field of 30 kV/m were generated at this time.
[0037] Subsequently, it was made for the pressure of the back section of the longitudinal direction X of said tubular member to serve as 4.5x10-4Torr using a header tank 2-1 and a pump 2-2. Furthermore, the coil 3 was made to generate the magnetic field of 0.01T for current in the longitudinal direction X of a sink and said tubular member.
[0038] The above conditions were held for 15 minutes, said CH4 gas plasma was introduced in said tubular member, chemical composition was performed, and the diamond-like carbon film was generated on the internal surface of said tubular member.
[0039] Drawing 2 is a graph which shows the Raman spectrum measured by the Raman spectroscopy of the diamond-like carbon film generated on the inner low wall surface of said tubular member. It turns out that the dispersion peak resulting from diamond-like carbon is observed, and the diamond-like carbon film made into the purpose on the internal surface of said tubular member is formed in about [ about 1360cm - ] 1 and about [ 1580cm - ] 1 in this example so that clearly from drawing 2 .
[0040] As mentioned above, although explained to details based on the gestalt of implementation of invention, giving an example, all modification and deformation are possible for this invention in the range which is not limited to the gestalt of implementation of the above-mentioned invention, and does not deviate from the criteria of this invention.
[0041]
[Effect of the Invention] He forms differential pressure before and after the longitudinal direction of a tubular member, and is trying to introduce plasma reactant gas in said tubular member using this differential pressure according to the thin film production method and thin film production equipment of this invention, as explained above. Therefore, a bore can form a predetermined thin film simply efficiently also to the internal surface of a very small tubular member. Moreover, the predetermined thin film made into the purpose also to the internal-surface top of two or more tubular members can be efficiently formed in coincidence.

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## DESCRIPTION OF DRAWINGS

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[Brief Description of the Drawings]
[Drawing 1] It is the schematic diagram showing an example of the thin film production equipment of this invention.
[Drawing 2] It is the graph which shows the Raman spectrum of the diamond-like carbon film produced according to the thin film production method and thin film production equipment of this invention.
[Description of Notations]
1 Membrane Formation Room, 2-1 Header Tank, 2-2 Pump, 3 Coil, 4-1 Anode Plate, 4-2 Cathode, 5 DC Power Supply, 6 High-Pressure Pulse Power Supply, 7 Gas Installation Hole, Eight Pumps, 9 Pressure Gage, 10 Aperture 20 Tubular Member

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DRAWINGS

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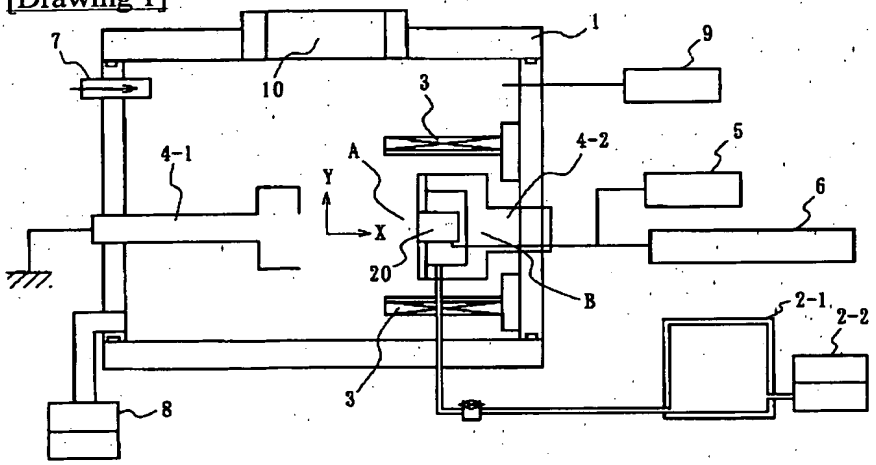
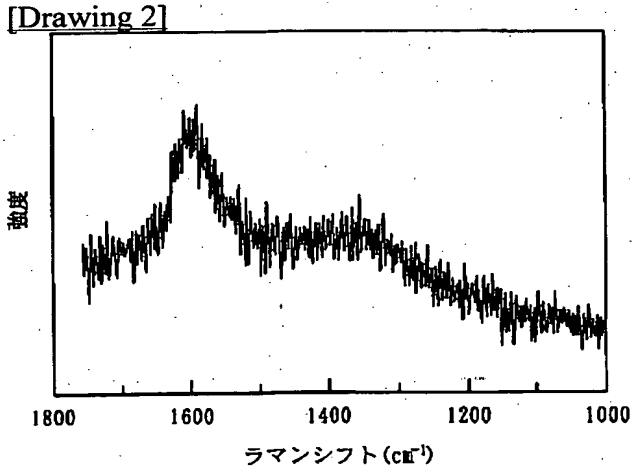
[Drawing 1]




[Drawing 2]

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| Ｃ０１Ｂ　31/02 | １０１ | Ｃ０１Ｂ　31/02 | １０１Ｚ | ４Ｋ０３０ |
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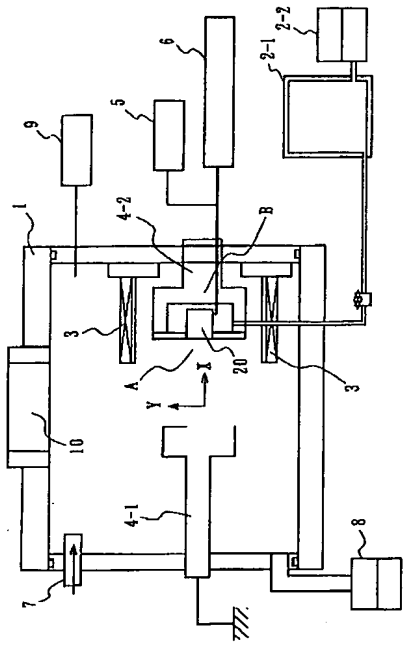
最終頁に続く

(54)【発明の名称】　薄膜作製方法及び薄膜作製装置

(57)【要約】
【課題】管状部材の内径の大きさやその数に依存することなく、極めて簡易に前記管状部材の内壁面上に薄膜を作製する手段を提供する。
【解決手段】管状部材２０の長手方向Ｘ後方部を、圧力調整槽２－１及びポンプ２－２から構成される圧力差生成手段２によって排気し、管状部材２０の長手方向Ｘ前方部の圧力に対して１０分の１以下の圧力に設定する。そして、ガス導入孔７から成膜室１内に導入された原料ガスに対して、ＤＣ電源５及び高圧パルス電源６より所定の電圧を印加することにより生成されたプラズマ反応ガスを、管状部材２０の長手方向Ｘにおける前方部及び後方部の圧力差を利用し、管状部材２０内に効率よく導入する。そして、管状部材２０の内壁面上において前記プラズマ反応ガスを化学的に合成させ、目的とする薄膜を形成する。



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【特許請求の範囲】

【請求項１】管状部材の内壁面上にプラズマＣＶＤにより薄膜を作製する方法であって、前記管状部材を所定のプラズマＣＶＤ装置内に配置するとともに、前記管状部材の長手方向前後において圧力差を生じさせ、プラズマ反応ガスを前記圧力差に応じて前記管状部材内に流入するようにし、前記管状部材の前記内壁面上において前記プラズマ反応ガスを化学的に合成させて前記薄膜を作製するようにしたことを特徴とする、薄膜作製方法。

【請求項２】前記管状部材の前記長手方向前後における圧力差は、前記長手方向後方部の圧力を前記長手方向前方部の圧力に対して１０分の１以下に設定することによって生じさせることを特徴とする、請求項１に記載の薄膜作製方法。

【請求項３】前記管状部材の前記長手方向において所定の磁場を生じさせ、前記プラズマ反応ガスを前記所定の磁場によって捕捉しながら前記管状部材内に流入させるようにしたことを特徴とする、請求項１又は２に記載の薄膜作製方法。

【請求項４】前記所定の磁場は、前記管状部材の前記長手方向と垂直な方向において、前記管状部材の内径よりも小さくなるように収束させることを特徴とする、請求項３に記載の薄膜作製方法。

【請求項５】前記所定の磁場の大きさが、前記管状部材の内径ｒに対して２．０×１０$^{-7}$／ｒＴ以上であることを特徴とする、請求項３又は４に記載の薄膜作製方法。

【請求項６】前記管状部材の前記長手方向において所定の電場を生じさせ、前記プラズマ反応ガスを前記所定の電場に従って前記管状部材内に流入させるようにしたことを特徴とする、請求項１～５のいずれか一に記載の薄膜作製方法。

【請求項７】前記所定の電場の大きさが、２０～２００ｋＶ／ｍであることを特徴とする、請求項６に記載の薄膜作製方法。

【請求項８】前記管状部材の前記内径は、０．００１～１ｍｍであることを特徴とする、請求項１～７のいずれか一に記載の薄膜作製方法。

【請求項９】前記薄膜は、ダイヤモンド又はダイヤモンド状炭素からなることを特徴とする、請求項１～８のいずれか一に記載の薄膜作製方法。

【請求項１０】管状部材の内壁面上にプラズマＣＶＤにより薄膜を作製する装置であって、所定のプラズマＣＶＤ装置に対して、前記管状部材の長手方向前後において圧力差を生じさせ、プラズマ反応ガスを前記圧力差に応じて前記管状部材内に流入するようにした圧力差生成手段を設けたことを特徴とする、薄膜作製装置。

【請求項１１】前記圧力差生成手段は、前記管状部材の前記長手方向後方部の圧力を前記長手方向前方部の圧力に対して１０分の１以下に設定することを特徴とする、

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請求項１０に記載の薄膜作製装置。

【請求項１２】前記所定のプラズマＣＶＤ装置に対して、前記管状部材の前記長手方向において所定の磁場を生じさせ、前記プラズマ反応ガスを前記所定の磁場によって捕捉しながら前記管状部材内に流入させるようにした磁場生成手段を設けたことを特徴とする、請求項１０又は１１に記載の薄膜作製装置。

【請求項１３】前記磁場生成手段は、前記所定の磁場を、前記管状部材の前記長手方向と垂直な方向において、前記管状部材の内径よりも小さくなるように収束させることを特徴とする、請求項１２に記載の薄膜作製装置。

【請求項１４】前記所定のプラズマＣＶＤ装置に対して、前記管状部材の前記長手方向において所定の電場を生じさせ、前記プラズマ反応ガスを前記所定の電場に従って前記管状部材内に流入させるようにした電場生成手段を設けたことを特徴とする、請求項１０～１３のいずれか一に記載の薄膜作製装置。

【発明の詳細な説明】

【０００１】

【発明の属する技術分野】本発明は、薄膜作製方法及び薄膜作製装置に関し、詳しくは、管状部材の内壁面に対する耐摩耗性薄膜コーティング手段として好適に用いることのできる薄膜作製方法及び薄膜作製装置に関する。

【０００２】

【従来の技術】所定の基材上に硬質膜、例えばダイヤモンド膜やダイヤモンド状炭素膜を形成し、前記所定の基材に対して耐摩耗性を付与することがことが行われている。そして、近年においては、数々の製品への応用が考えられる管状部材の内壁面に対して前記硬質膜を形成する試みがなされている。

【０００３】硬質膜の形成は、例えば、メタンガスなどの原料ガスを水素ガスなどのキャリアガスなどとともにプラズマ反応炉内に導入し、マイクロ波、高周波などによって前記原料ガスを励起してプラズマ反応ガスを生成し、前記所定の基材上において化学的な反応を行わせる、いわゆるプラズマＣＶＤ法を用いて実施される。しかしながら、プラズマＣＶＤ法は、板状部材やその他簡易な形状の部材に対しては所定の硬質膜を均一に形成することができるが、管状部材の内壁面など複雑な形状の部材に対しては、各構成部分に対する前記プラズマ反応ガスの回り込みが不十分となるため、均一な硬質膜を形成することができないでいた。

【０００４】かかる点に鑑みて、特開昭６２－１３６５６９号公報においては、管状部材の内部に黒鉛材からなる電極を配置し、前記管状部材の内部で原料ガスからプラズマ反応ガスを直接的に形成することが試みられている。この方法によれば、前記管状部材の内壁面上に多量の前記プラズマ反応ガスを供給することができるため、前記内壁面上においても、比較的厚い硬質膜を簡易かつ

均一に形成することができる。

【０００５】

【発明が解決しようとする課題】しかしながら、上記方法においては、管状部材の内径よりも小さな黒鉛電極を準備する必要があり、前記管状部材の内径が極めて小さくなるとその作製が極めて困難になる。また、複数の管状部材を準備し、これらの内壁面上に対して同時に硬質膜を形成しようとすると、前記管状部材の数に応じた黒鉛電極を準備する必要が生じる。この結果、プラズマＣＶＤ装置全体の構成が複雑になるとともに、硬質膜の作製工程が極めて複雑になるという問題があった。

【０００６】本発明は、管状部材の内径の大きさやその数に依存することなく、極めて簡易に前記管状部材の内壁面上に薄膜を作製する手段を提供することを目的とする。

【０００７】

【課題を解決するための手段】上記目的を達成すべく、本発明は、開口部が形成された底面を有する管状部材の内壁面上に、プラズマＣＶＤにより薄膜を作製する方法であって、前記管状部材を所定のプラズマＣＶＤ装置内に配置するとともに、前記管状部材の長手方向前後において圧力差を生じさせ、プラズマ反応ガスを前記圧力差に応じて前記管状部材内に流入するようにし、前記管状部材の前記内壁面上において前記プラズマ反応ガスを化学的に合成させて前記薄膜を作製するようにしたことを特徴とする、薄膜作製方法に関する。

【０００８】また、本発明は、開口部が形成された底面を有する管状部材の内壁面上に、プラズマＣＶＤにより薄膜を作製する装置であって、所定のプラズマＣＶＤ装置に対して、前記管状部材の長手方向前後において圧力差を生じさせ、プラズマ反応ガスを前記圧力差に応じて前記管状部材内に流入するようにした圧力差生成手段を設けたことを特徴とする、薄膜作製装置に関する。

【０００９】本発明者らは、上記目的を達成すべく鋭意検討を実施した。その結果、所定の薄膜を形成すべき管状部材の長手方向前後において圧力差を形成し、この圧力差を利用して前記管状部材内に所定の原料ガスを励起して得たプラズマ反応ガスを流入させることにより、上記目的を達成できることを見出した。

【００１０】すなわち、従来のプラズマＣＶＤ法においては、前記所定の原料ガスを装置内に導入し、励起してプラズマ反応ガスを生成させた後は、前記原料ガスの対流によって前記プラズマ反応ガスを所定の箇所、例えば管状部材の内壁面上に供給していた。これに対して、本発明の薄膜作製方法及び薄膜作製装置によれば、上述したように、圧力差生成手段によって、前記管状部材の長手方向前後において圧力差を設けるようにしている。

【００１１】したがって、従来の対流を利用したプラズマＣＶＤ法に比べて多量のプラズマ反応ガスを前記管状部材の内壁面上に供給することができる。この結果、前記管状部材の内壁面上において、前記プラズマ反応ガスを十分に化学的に反応させることができ、目的とする薄膜を簡易に形成することができる。

【００１２】このように本発明の薄膜作製方法及び薄膜作製装置によれば、圧力差を利用してプラズマ反応ガスを管状部材内に導入するので、前記管状部材の内径が十分に小さい場合においても、前記プラズマ反応ガスを高効率に導入して、内壁面上に対して簡易に薄膜形成を行うことができる。

【００１３】また、管状部材毎に電極などを設ける必要がないので、複数の管状部材の内壁面上に目的とする薄膜を同時に形成することができ、薄膜作製効率を大きく向上させることができる。

【００１４】本発明の好ましい態様においては、磁場生成手段を設け、前記管状部材の長手方向において所定の磁場を生じさせ、前記プラズマ反応ガスを前記所定の磁場によって捕捉しながら前記管状部材内に流入させることが好ましい。これによって、プラズマ反応ガスの管状部材内への流入割合が増大するため、前記管状部材内に前記プラズマ反応ガスをより効率よく導入することができる。

【００１５】さらに、本発明に他の好ましい態様においては、電場生成手段を設け、前記管状部材の長手方向において所定の電場を生じさせ、前記プラズマ反応ガスを前記所定の電場に従って前記管状部材内に導入することが好ましい。この場合においても、前記プラズマ反応ガスの前記管状部材内への流入割合が増大するため、前記管状部材内に前記プラズマ反応ガスをより効率良く導入することができる。

【００１６】なお、上記電場生成手段によって前記原料ガスの励起を実施し、プラズマ反応ガスを生成することもできる。この場合においては、プラズマ反応ガスを生成するために追加の励起手段を設ける必要がないため、装置全体の構成が簡易化されるとともに、薄膜作製工程を簡易化することができる。

【００１７】

【発明の実施の形態】以下、本発明を、図面と関連させながら、発明の実施の形態に基づいて詳細に説明する。

【００１８】図１は、本発明の薄膜作製装置の一例を示す図である。図１に示す薄膜作製装置は、成膜室１と、この成膜室１に接続して設けられた圧力差生成手段としての圧力調整槽２－１及びポンプ２－２と、磁場生成手段としてのコイル３と、電場生成手段としての陽極４－１及び陰極４－２とを具えている。陽極４－１は接地され、陰極４－２にはＤＣ電源５及び高圧パルス電源６が接続されている。

【００１９】また、成膜室１には所定の原料ガスを導入するためのガス導入孔７及び成膜室１内を所定の真空度に保持するべく、排気手段としてのポンプ８が設けられている。さらに、圧力計９及び窓１０が設けられ、成膜

室１内の真空度及びプラズマ反応ガスの状態を常時モニターできるように構成されている。管状部材２０は陰極４－２の上方において固定され、設置されている。

【００２０】管状部材２０の内壁面上への薄膜作製は以下のようにして実施する。

【００２１】最初に、成膜室１内をポンプ８によって所定の真空度まで排気した後、ガス導入孔７より所定の原料ガスを成膜室１内に供給する。そして、ポンプ８による排気と相伴って、成膜室１内を所定の真空度に保持する。なお、真空度は成膜室１に設けられた圧力計９によってモニターする。

【００２２】次いで、ＤＣ電源５によって所定のＤＣバイアスを印加しながら、高圧パルス電源６より所定のパルス電圧を印加することによって、前記原料ガスを励起してプラズマ反応ガスを生成する。

【００２３】次いで、ポンプ２－２より圧力調整層２－１を介して管状部材２０が設置された陰極４－２周囲を排気し、管状部材２０の長手方向Ｘの前後において圧力差を生じさせる。管状部材２０の長手方向Ｘ前後における圧力差は、管状部材２０の長手方向Ｘの後方部における圧力が、長手方向Ｘの前方部における圧力の１０分の１以下、さらには１００分の１以下となるように設定することが好ましい。これによって、前記プラズマ反応ガスをより効率的に管状部材２０内に導入することができる。

【００２４】具体的には、成膜室１内の圧力は約$10^{-2}$Ｔｏｒｒ前後であり、管状部材２０の長手方向Ｘの前方部Ａの圧力も約$10^{-2}$Ｔｏｒｒ前後となるので、管状部材の長手方向Ｘの後方部Ｂの圧力は、約$10^{-3}$～$10^{-4}$Ｔｏｒｒになるように圧力調整槽２－１及びポンプ２－２によって制御する。

【００２５】次いで、コイル３に対して電流を流すことにより、管状部材２０の長手方向Ｘにおいて所定の磁場を生成させる。そして、この磁場は、管状部材２０の長手方向Ｘと垂直なＹ方向において、管状部材２０の内径より小さくなるように収束させることが好ましい。これによって、前記プラズマ反応ガスの管状部材２０内への流入割合をより増大させることができ、管状部材２０の内壁面上への薄膜形成をより簡易かつ効率的に実施することができる。

【００２６】また、前記所定の磁場の大きさは、管状部材2.0の内径をｒとした場合において、$2.0\times10^{-7}$／ｒＴであることが好ましい。具体的には、管状部材２０の内径ｒが１．０ｍｍである場合においては、$1.0\times10^{-4}$～$3.0\times10^{-4}$Ｔであることが好ましく、さらには$2.0\times10^{-4}$～$3.0\times10^{-4}$Ｔであることが好ましい。これによって、前記プラズマ反応ガスの捕捉をより効果的に実施することができ、管状部材２０内への前記プラズマ反応ガスの流入割合が増大するため、前述したように、管状部材２０の内壁面上への薄膜形成をより簡易かつ効率的に実施することができる。



【００２７】さらに、陰極４－２から陽極４－１に向かっては、前記原料ガスを励起してプラズマ反応ガスを生成するためのＤＣバイアス及びパルス電圧に起因して所定の電場が生成されている。したがって、前記プラズマ反応ガスは、前記所定の電場にしたがって管状部材２０内に流入するようになる。この結果、前記プラズマ反応ガスの管状部材２０内への流入割合が増大し、管状部材２０の内壁面上への薄膜形成をより効率的に行うことができる。

【００２８】前記所定の電場の大きさは、２０～２００ｋＶ／ｍであることが好ましく、さらには２０～１００ｋＶ／ｍであることが好ましい。図１に示す薄膜作製装置においては、原料ガスからプラズマ反応ガスを生成すべく、ＤＣ電源５及び高圧パルス電源６から陰極４－２に印加される電圧値はほぼある範囲内に定められるが、この範囲内において前記電圧値を適宜に調節し、前記所定に電場の大きさが上記範囲内の値となるように設定する。

【００２９】以上説明したように、図１に示す薄膜作製装置によれば、管状部材２０の長手方向Ｘの前後において圧力差を設けるのみでなく、長手方向Ｘに沿って前記所定の磁場及び前記所定の電場を発生させるようにしているので、前記プラズマ反応ガスを極めて効率良く管状部材２０内に流入させることができる。したがって、管状部材２０の内壁面上において極めて効率良く所定の薄膜を形成することができる。

【００３０】本発明の薄膜作製方法及び薄膜作製装置は、管状部材２０の形状及び大きさについては限定されず、あらゆる形状及び大きさの管状部材に対して適用することができる。また、管状部材２０は、圧力差に応じた内部プラズマ反応ガスの流入が阻止されないように、開口部が形成された底面を有することもできる。かかる底面を管状部材２０の長手方向Ｘの後方部に対して設けた場合は、前記底面の内壁面に対するプラズマ反応ガスの供給量が増大するために、前記底面の前記内壁面において目的とする薄膜を比較的厚く、効率良く形成することができる。

【００３１】しかしながら、このような場合においても、管状部材の大きさに合わせて、圧力差の制御及び磁場の制御を適宜に行うことにより、管状部材２０の内側壁面上においても十分な厚さの薄膜を効率よく形成することができ、これによって、内側壁面上及び内底壁面上において均一かつ効率よく目的とする薄膜を形成することができる。

【００３２】本発明の薄膜作製方法及び薄膜作製装置によれば、内径１０ｍｍ以下、さらには１ｍｍ以下の管状部材の内壁面上にまで目的とする薄膜を効率良く形成することができる。また、現状においては、内径０．０１

ｍｍ以上、特には０．１ｍｍ以上の管状部材の内壁面上に目的とする薄膜を効率良く形成することができる。

【００３３】また、本発明の薄膜作製方法及び薄膜作製装置においては、上述したように圧力差を用いて薄膜の形成を行っており、管状部材毎に電極などを設ける必要がないので、図１において、管状部材２０を複数配置した場合においても、これら複数の管状部材の内壁面上に目的とする薄膜を同時に形成することができる。したがって、薄膜の作製効率を極めて高くすることができる。

【００３４】また、管状部材２０の内壁面上に形成する薄膜の種類についても特には限定されない。しかしながら、前記薄膜をダイヤモンド又はダイヤモンド状炭素から構成することによって、管状部材２０の内壁面に高い摩耗性を付与することができる。したがって、管状部材２０を所定の摺動部材として使用することができる。

【００３５】

【実施例】以下、実施例により本発明を具体的に説明する。

（実施例）本実施例においては、底面側に高さ０．１ｍｍ、幅４０ｍｍのスリット型開口部が形成された、内径１ｍｍの管状部材の内壁面上に、図１に示すような作製装置を用いてダイヤモンド状炭素膜を形成することを試みた。

【００３６】最初に、前記管状部材を陰極４－２の上方に固定して設置した後、成膜室１内をポンプ８によって$10^{-5}$ Ｔｏｒｒの真空度まで排気した。そして、ガス導入孔７よりＣＨ$_4$ ガスを２０ｃｍ$^3$ ／ｍｉｎの流量で導入し、ポンプ８で排気しながら成膜室１内の圧力を$3.75\times10^{-2}$ Ｔｏｒｒに設定した。次いで、ＤＣ電源５及び高圧パルス電源６より陽極４－１及び陰極４－２間に１．５ｋＶの電圧を印加し、ＣＨ$_4$ ガスプラズマを生成させた。なお、このとき陽極４－１及び陰極４－２間には３０ｋＶ／ｍの電場が生成された。

【００３７】次いで、圧力調整槽２－１及びポンプ２－２を用いて前記管状部材の長手方向Ｘの後方部の圧力が$4.5\times10^{-4}$ Ｔｏｒｒとなるようにした。さらに、コイル３に電流を流し、前記管状部材の長手方向Ｘにおいて、０．０１Ｔの磁場を発生させた。



【００３８】上述のような状態を１５分間保持し、前記ＣＨ$_4$ ガスプラズマを前記管状部材内に導入し、化学的な合成を行って、前記管状部材の内壁面上にダイヤモンド状炭素膜を生成した。

【００３９】図２は、前記管状部材の内低壁面上に生成したダイヤモンド状炭素膜のラマン分光法によって測定したラマンスペクトルを示すグラフである。図２から明らかなように、約１３６０ｃｍ$^{-1}$ 近傍及び１５８０ｃｍ$^{-1}$ 近傍にダイヤモンド状炭素に起因した散乱ピークが観察され、本実施例において、前記管状部材の内壁面上に目的とするダイヤモンド状炭素膜が形成されていることが分かる。

【００４０】以上、具体例を挙げながら、発明の実施の形態に基づいて詳細に説明したが、本発明は上記発明の実施の形態に限定されるものではなく、本発明の範疇を逸脱しない範囲であらゆる変更や変形が可能である。

【００４１】

【発明の効果】以上説明したように、本発明の薄膜作製方法及び薄膜作製装置によれば、管状部材の長手方向前後に圧力差を形成し、この圧力差を利用してプラズマ反応ガスを前記管状部材内に導入するようにしている。したがって、内径が極めて小さい管状部材の内壁面に対しても所定の薄膜を効率良く簡易に形成することができる。また、複数の管状部材の内壁面上に対しても目的とする所定の薄膜を同時に効率よく形成することができる。

【図面の簡単な説明】

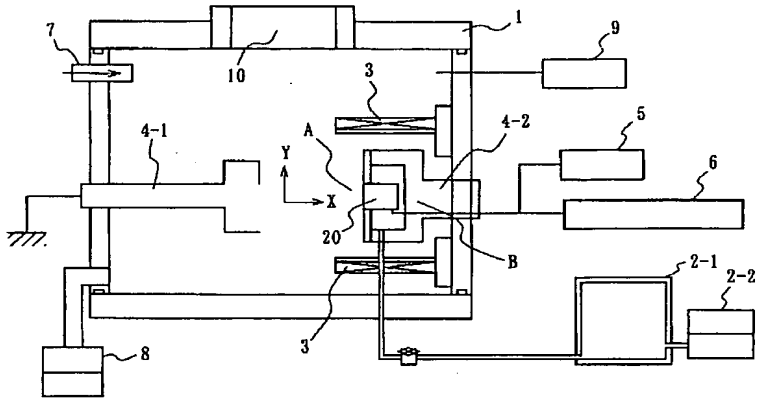
【図１】本発明の薄膜作製装置の一例を示す概略図である。

【図２】本発明の薄膜作製方法及び薄膜作製装置に従って作製したダイヤモンド状炭素膜の、ラマンスペクトルを示すグラフである。

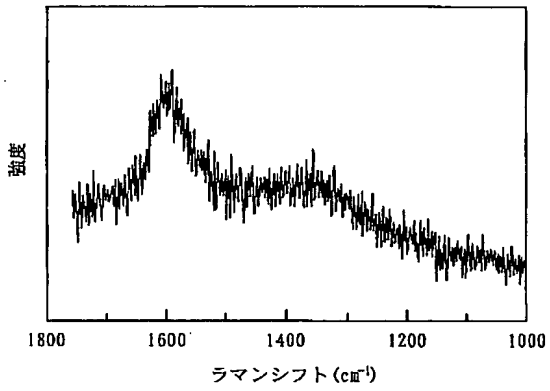
【符号の説明】

１　成膜室、２－１　圧力調整槽、２－２　ポンプ、３　コイル、４－１　陽極、４－２　陰極、５　ＤＣ電源、６　高圧パルス電源、７　ガス導入孔、８ポンプ、９　圧力計、１０　窓、　２０　管状部材

【図１】




【図２】

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